The exact Hohenberg-Kohn functional for a lattice model

Tanja Dimitrov[1] (dimitrov@fhi-berlin.mpg.de), Heiko Appel[1], Angel Rubio[1,2]

[1] Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany
[2] NanoBio Spectroscopy group and ETSF, Universidad del País Vasco, San Sebastián, Spain

MAX-PLANCK-GESELLSCHAFT

Introduction

For a discretized soft-Coulomb lattice model, we investigate the exact solution of the many-body Schrödinger equation in Fock space. Using quadratic optimization with quadratic constraints, or alternatively exact diagonalization, we explicitly construct the exact Hohenberg-Kohn functional and the mapping from densities to wavefunctions. We analyze the resulting exact Hohenberg-Kohn functional and draw conclusions for the construction of approximate functionals.

Two-site soft-Coulomb model

$$\hat{H} = \hat{T} + \hat{W} + \hat{V}, \quad \hat{T} = -t_0 \sum_{l,\sigma} (\hat{c}^\dagger_{l,\sigma}\hat{c}_{l+1,\sigma} + \hat{c}^\dagger_{l+1,\sigma}\hat{c}_{l,\sigma}) + 2t_0 \sum_{l,\sigma} \hat{n}_{l,\sigma}, \quad t_0 = \frac{\hbar^2}{2m_e\Delta^2},$$

$$\hat{W}_{\mathrm{H}} = U \sum_l \hat{n}_{l,\uparrow}\hat{n}_{l,\downarrow}, \quad \hat{W}_{\mathrm{SC}} = \sum_{l,m,\sigma,\sigma'} \frac{e^2 \hat{c}^\dagger_{l,\sigma}\hat{c}^\dagger_{m,\sigma'}\hat{c}_{m,\sigma'}\hat{c}_{l,\sigma}}{2\sqrt{(l\Delta - m\Delta)^2+1}}, \quad \hat{V} = \sum_{l,\sigma} \hat{n}_{l\sigma}\cdot v_{l,\sigma}, \quad \hat{n} = \sum_{j,\sigma} \hat{c}^\dagger_{j,\sigma}\hat{c}_{j,\sigma}$$

We consider different particle numbers by including a chemical potential μ. Spacing Δ

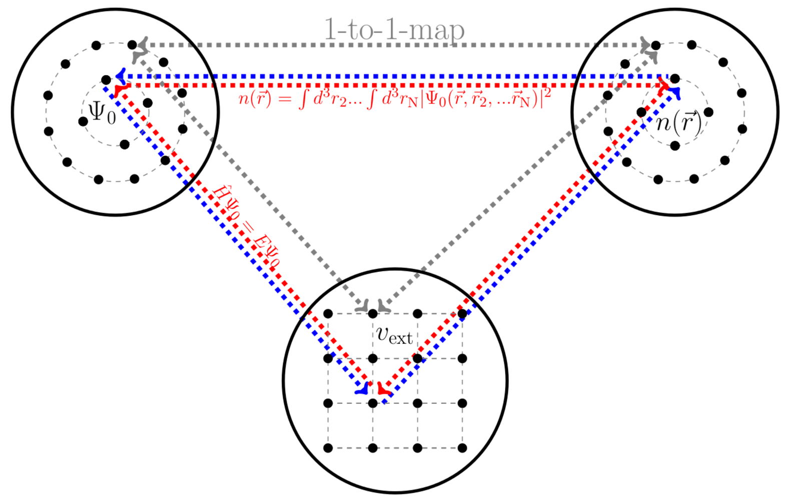
Levy-Lieb constraint search (M. Levy 1979 [1], E. Lieb 1983 [2])

Expand eigenfunctions in a complete basis set (energy eigenfunctions, Slater-Determinants, etc.)

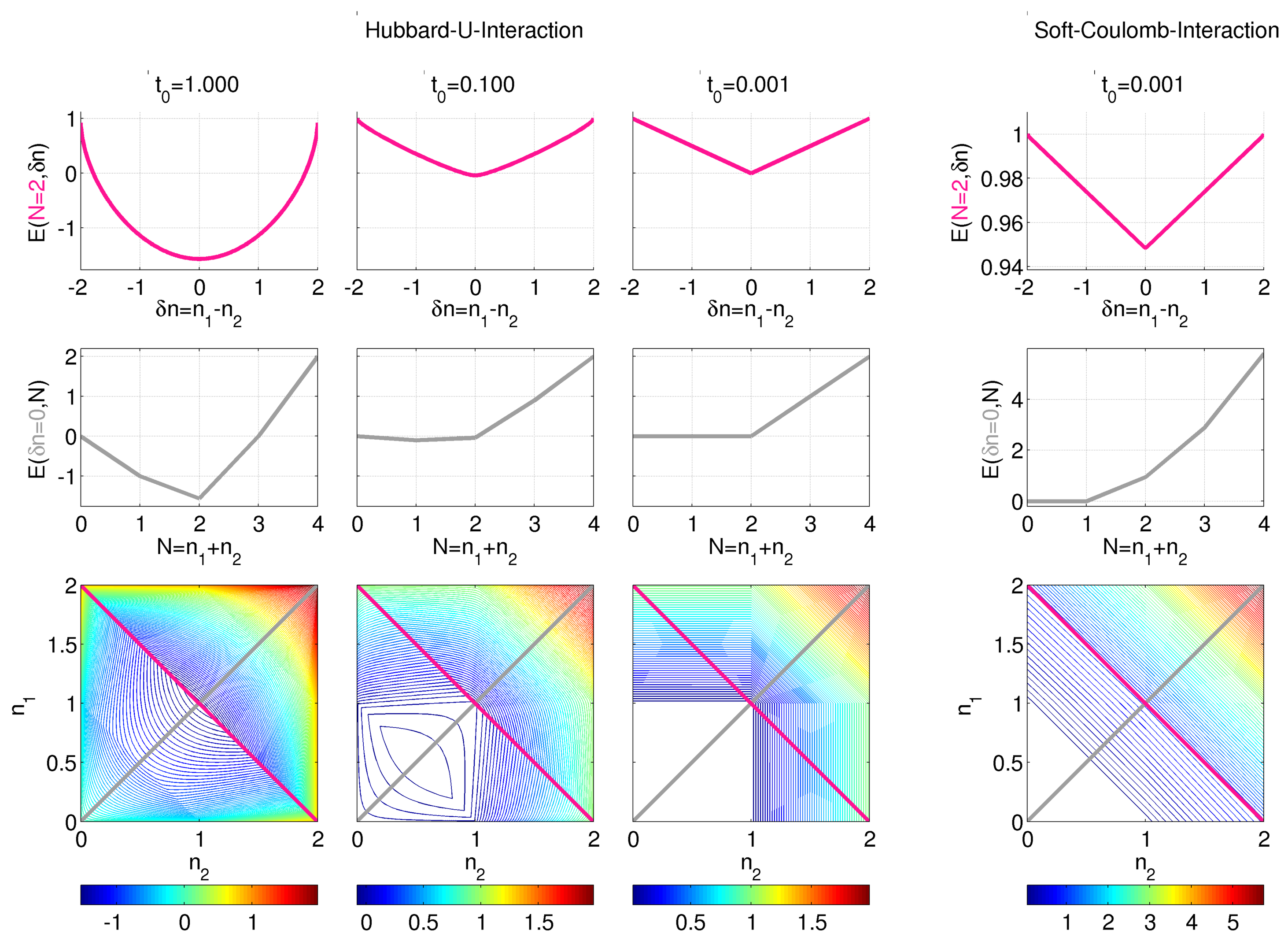
$$|\,\Psi[n]\,\rangle = \sum_{j=1}^{4^M} \alpha_j[n]\,|\,\phi_j\,\rangle\,, \text{ M number of sites}$$

Hohenberg-Kohn functional

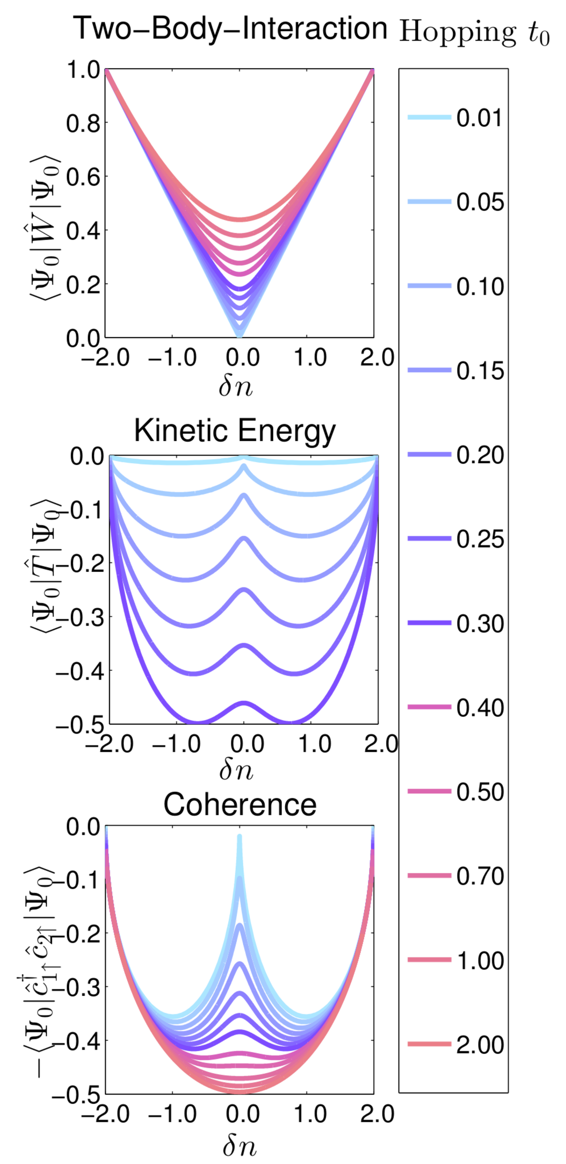
$$\begin{aligned} F_{\mathrm{HK}}(\alpha_1, ..., \alpha_{4^M})[n] &= \min_{\Psi\to n} \langle\,\Psi[n]\,|\,\hat{T}+\hat{W}\,|\,\Psi[n]\,\rangle \\ &= \min_{\Psi\to n} \sum_{j,k=1}^{4^M} \alpha_j^*[n]\alpha_k[n]\,\langle\,\phi_j\,|\,\hat{T}+\hat{W}\,|\,\phi_k\,\rangle \end{aligned}$$



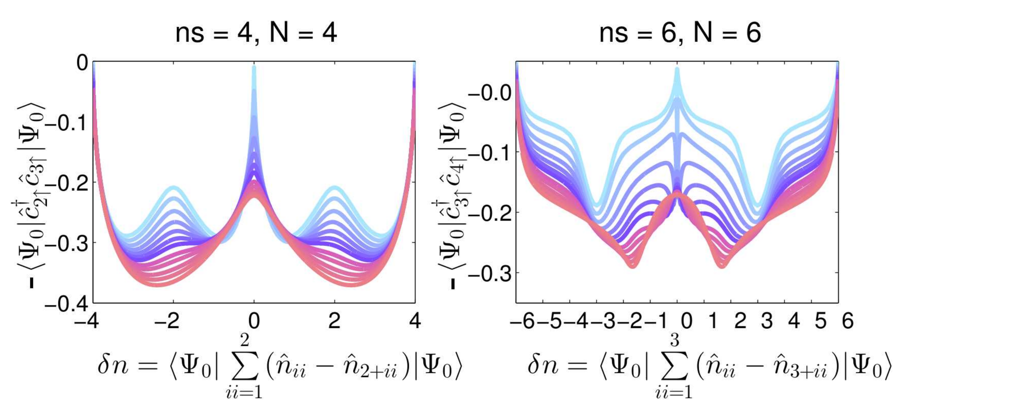
Exact Hohenberg-Kohn-Functional



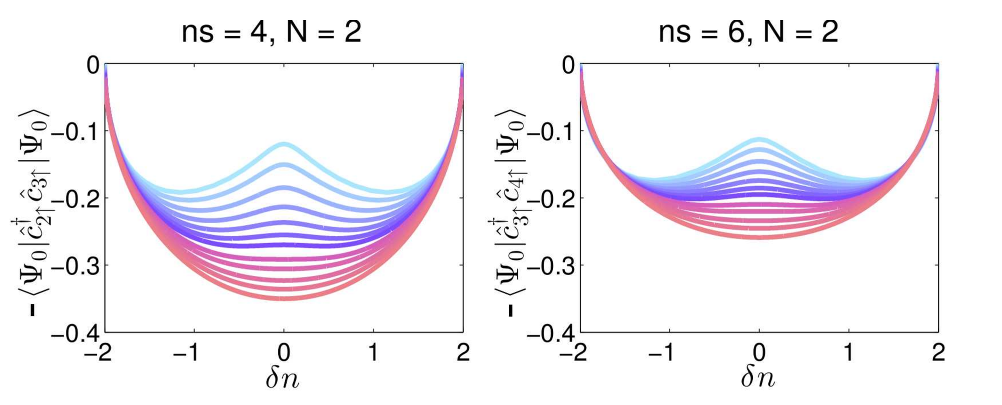
Exact Coherences



Coherences for ns = 4 and ns = 6 (half-filling)



Coherences for ns = 4 and ns = 6 (N=2)



Soft-Coulomb molecules in 1D

Hamiltonian

$$\hat{H}(\alpha) = \hat{T} + \hat{W} + \hat{V}(\alpha)$$

$$\hat{T} = \sum_{j=1}^{2} -\frac{d^2}{dx_j^2}, \; \hat{W} = \frac{1}{2}\sum_{i\neq j}^{2} \frac{1}{\sqrt{(x_i-x_j)^2+1}}$$

$$\hat{V}(\alpha) = \sum_{j=1}^{2} \frac{Z_1(\alpha)}{\sqrt{(x_j-d)^2+1}} + \frac{Z_2(\alpha)}{\sqrt{(x_j+d)^2+1}}$$

$$Z_1(\alpha) = -\alpha, \quad Z_2(\alpha) = -(2-\alpha), \quad \alpha\in[0,2], \quad d = 3, 8 \text{ Bohr}$$

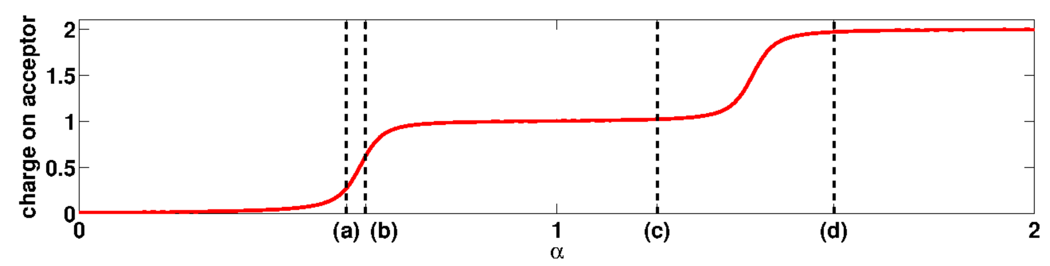
Exact Kohn-Sham potential for two electrons in spin singlet configuration (Helbig et al. 2009 [3])

$$v_{\mathrm{KS}}(x) = \frac{1}{2}\frac{\nabla^2\sqrt{n(x)}}{\sqrt{n(x)}} + \epsilon_1$$

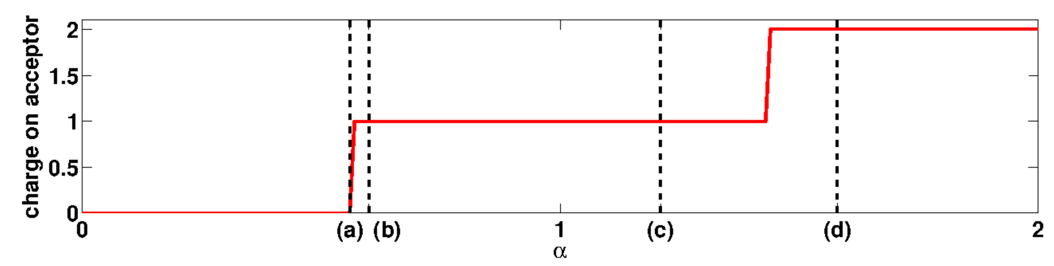
Exact solution of static two-electron Schrödinger equation with octopus (A. Castro et al. [4])

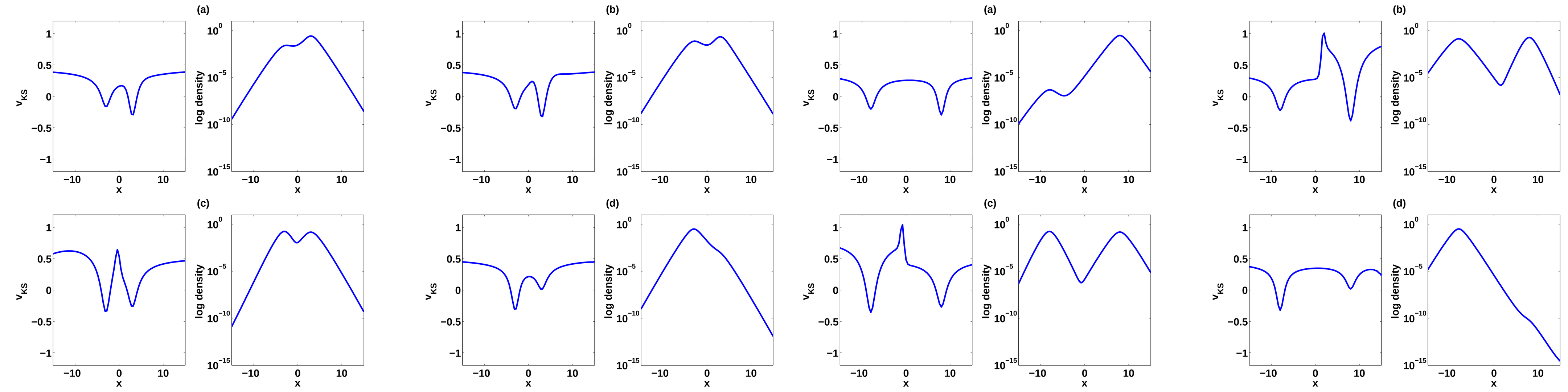
$$\begin{aligned} \hat{H}(\alpha)\Psi_j(\alpha) &= E_j(\alpha)\Psi_j(\alpha) \\ n(x) &= \langle\,\Psi\,|\,\hat{n}(x)\,|\,\Psi\,\rangle \\ \hat{n}(x) &= \sum_j \delta(x - x_j) \end{aligned}$$

High-density limit (small distance $d = 3$ Bohr)

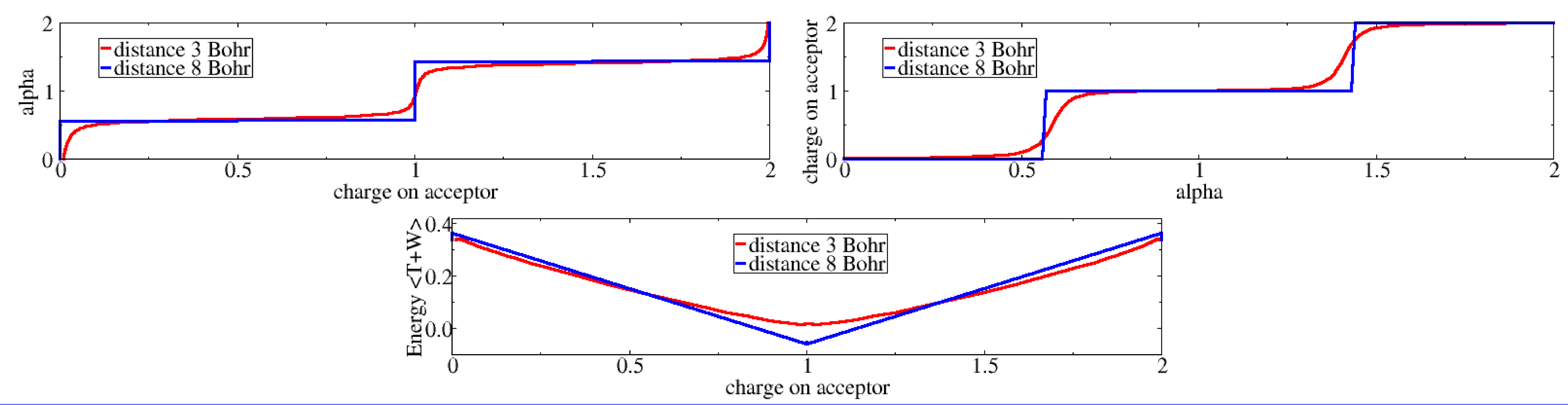


Low-density limit (large distance $d = 8$ Bohr)





Softened intra-system derivative discontinuity



Conclusion & Outlook

- The exact Hohenberg-Kohn functional shows a softened intra-system derivative discontinuity in the low-density limit.
- Expectation values of operators are affected by the softened intra-system derivative discontinuity.
- We observe softened intra-system derivative discontinuity also for soft-Coulomb molecules in 1D.
- We currently develop an approximate functional which incorporates the intra-system derivative discontinuity.

References

[1] M. Levy, Proc. Natl Acad. Sci. USA 76 6062 (1979)

[2] E. Lieb, Int. J. Quantum Chem. 24 24377 (1983)

[3] N. Helbig, I.V. Tokatly, A. Rubio, Journal of Chemical Physics 131, 224105 (2009)

[4] A. Castro, H. Appel, Micael Oliveira, C.A. Rozzi, X. Andrade, F. Lorenzen, M.A.L. Marques, E.K.U. Gross, and A. Rubio, Phys. Stat. Sol. B 243 2465-2488 (2006)

[5] John P. Perdew, Robert G. Parr, Mel Levy, Jose L. Balduz, Jr., Phys. Rev. Lett. 49, 16911694 (1982)